Density Scaling and Virial Theorem

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Abstract

The virial theorem, the Levy-Perdew relation and the differential virial theorem are derived for density scaled Kohn-Sham systems. Earlier it was shown that there exists a value of the scaling factor for which the correlation energy disappears and we should treat only exchange for which a simple approximation was proposed. The new Levy-Perdew relation is applied to judge the quality of this approximation.

I. INTRODUCTION

This paper is dedicated to the memory of Nicholas Handy. He was an outstanding scientist, he had very important contributions to several fields of quantum chemistry. Among others, he emphasized the importance of density scaling [1] in the density functional theory. This paper can be considered as a continuation of his ideas: the derivation of the virial theorem for the scaled energy components.

A kind of scaling, the so-called coordinate scaling has been applied in density functional theory for decades. The functionals expressed with the scaled density $\varrho_\lambda(\mathbf{r}) = \zeta^3\varrho(\lambda\mathbf{r})$ should satisfy several important relations[2, 3] that turned to be very useful in constructing and improving approximate functionals.

The density scaling proposed by Chan and Handy [1] is another type of scaling, where the density is multiplied by a positive real number ζ, that is, $\varrho(\mathbf{r}) \to \zeta\varrho(\mathbf{r})$. Several studies [4–14] utilized it in density functional theory. Zhao, Morrison, and Parr had previously investigated closely related homogeneity relations between the functionals [15–17]. In this paper the virial theorem will be in the focus.

II. DENSITY SCALING

In the density functional theory [18] we generally use the Kohn-Sham scheme [19], where the Kohn-Sham equations

$$\left[-\frac{1}{2}\nabla^2 + v_{KS}(\mathbf{r})\right]\phi_i = \varepsilon_i\phi_i \tag{1}$$

are solved with the Kohn-Sham potential

$$v_{KS}(\mathbf{r}) = v(\mathbf{r}) + v_J(\mathbf{r}) + v_{xc}(\mathbf{r}). \tag{2}$$

ϕ_i, ε_i, v, v_J and v_{xc} are the orbitals, orbital energies, the external potential, the classical Coulomb potential and the exchange-correlaton potential, respectively. The total energy can be given by the quantities defined in the Kohn-Sham theory, namely,

$$E[\varrho] = T_s[\varrho] + J[\varrho] + E_{xc}[\varrho] + \int \varrho(\mathbf{r})v(\mathbf{r})d\mathbf{r}, \tag{3}$$

where T_s, E_{xc} and

$$J[\varrho] = \frac{1}{2}\int \frac{\varrho(\mathbf{r}_1)\varrho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}d\mathbf{r}_1 d\mathbf{r}_2 \tag{4}$$

are the non-interacting kinetic energy, the exchange-correlation energy and the classical Coulomb energy, respectively.

Now, a "scaled" Kohn-Sham system is introduced that corresponds to the scaled density $\varrho_\zeta(\mathbf{r}) = \varrho(\mathbf{r})/\zeta$. Due to the scaling the particle number changes, too: $N_\zeta = N/\zeta$. As we now generally have noninteger particle numbers, density matrices [1] should be applied in the derivation of the "scaled" Kohn-Sham equation. Then the "scaled" kinetic energy and the scaled density read as

$$T_\zeta[\varrho] = \min_{\zeta \sum_i^M \lambda_i |\phi_{\zeta i}|^2 \to \varrho} \left[-\frac{1}{2} \zeta \sum_i^M \lambda_i \langle \phi_{\zeta i} | \nabla_i^2 | \phi_{\zeta i} \rangle \right]. \tag{5}$$

and

$$\varrho_\zeta(\mathbf{r}) = \sum_i^M \lambda_i |\phi_{\zeta i}(\mathbf{r})|^2, \tag{6}$$

where λ_i are the occupation numbers and M is the number of orbitals with non-zero occupation number. The minimization of the "scaled" kinetic energy leads to the "scaled" Kohn-Sham equations

$$\left[-\frac{1}{2} \nabla^2 + v_{\zeta KS}(\mathbf{r}) \right] \phi_{\zeta i} = \varepsilon_{\zeta i} \phi_{\zeta i}, \tag{7}$$

where the "scaled" Kohn-Sham potential has the form

$$v_{\zeta KS}(\mathbf{r}) = v(\mathbf{r}) + v_J(\mathbf{r}) + v_{\zeta xc}(\mathbf{r}). \tag{8}$$

$v_{\zeta xc}$ is the "scaled" exchange-correlaton potential. The total energy has a new partition:

$$E[\varrho] = T_\zeta[\varrho] + J[\varrho] + E_{\zeta xc}[\varrho] + \int \varrho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r}, \tag{9}$$

where the "scaled" exchange-correlation energy $E_{\zeta xc}[\varrho]$ is defined by Eq. (9) and the functional derivative of $E_{\zeta xc}[\varrho]$ is the "scaled" exchange-correlaton potential $v_{\zeta xc}$. Note that there is no ζ dependence in the classical Coulomb and external energy parts, only the kinetic energy and the exchange-correlation energy are scaled. It means that the scaling does not change the sum of the kinetic and the exchange-correlation energies. From Eqs. (3) and (9) we arrive at the significant relations

$$T_s[\varrho] + E_{xc}[\varrho] = T_\zeta[\varrho] + E_{\zeta xc}[\varrho] \tag{10}$$

and

$$\frac{\delta T_s[\varrho]}{\delta \varrho} + v_{xc}(\mathbf{r}) = \frac{\delta T_\zeta[\varrho]}{\delta \varrho} + v_{\zeta xc}(\mathbf{r}). \tag{11}$$

Eq. (10) reflects that the density scaling either increases the kinetic part and decreases the exchange-correlation term or vice-versa.

III. VIRIAL THEOREM

The virial theorem of quantum mechanics in case of Coulomb potential in equilibrium molecular geometry has the form

$$T = -E \ , \tag{12}$$

where T and E are the kinetic and total energies, respectively. In the Kohn-Sham scheme of the density functional theory it can be written as [2]

$$T_s + T_c = -E \tag{13}$$

as the non-interacting kinetic energy T_s differs from the interacting kinetic energy T. As the difference T_c is positive the inequality $T_s < -E$ holds.

Using the "scaled" Kohn-Sham scheme we can write

$$T_\zeta + T_{c\zeta} = -E \tag{14}$$

instead of Eq. (13).

Now, use the operator $\mathbf{r} \cdot \nabla$ on the "scaled" Kohn-Sham equations (7), multiply by $\lambda_i \phi^*_{\zeta i}$, integrate and sum for all orbitals. Then we are led to the virial theorem

$$T_\zeta = \frac{1}{2} \int \varrho \mathbf{r} \cdot \nabla v_{KS}(\mathbf{r}) d\mathbf{r}. \tag{15}$$

Using the partition of the "scaled" Kohn-Sham potential (8) and the identities

$$J = -\int \varrho(\mathbf{r}) \mathbf{r} \cdot \nabla v_J(\mathbf{r}) d\mathbf{r} \ , \tag{16}$$

$$\int \varrho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} = -\int \varrho(\mathbf{r}) \mathbf{r} \cdot \nabla v(\mathbf{r}) \tag{17}$$

in equilibrium, we obtain

$$2T_\zeta[\varrho] = -J[\varrho] - \int \varrho(\mathbf{r})v(\mathbf{r})d\mathbf{r} + \int \varrho(\mathbf{r})\mathbf{r}\cdot\nabla v_{\zeta xc}(\mathbf{r}). \tag{18}$$

Making use of Eqs. (9) and (14), Eq. (18) leads to the "scaled" Levy-Perdew relation

$$T_{c\zeta} + E_{\zeta xc} = -\int \varrho\mathbf{r}\cdot\nabla v_{\zeta xc}(\mathbf{r})d\mathbf{r}\ . \tag{19}$$

IV. DIFFERENTIAL VIRIAL THEOREM

The differential virial theorem was derived by Holas and March [20] in the density functional theory. Now it is extended to the "scaled" Kohn-Sham scheme. The "scaled" Kohn-Sham equations (7) can be rewritten as

$$v_{\zeta KS} - \varepsilon_{\zeta i} = \frac{1}{2}\frac{\nabla^2\phi_{\zeta i}^{Re}}{\phi_{\zeta i}^{Re}} = \frac{1}{2}\frac{\nabla^2\phi_{\zeta i}^{Im}}{\phi_{\zeta i}^{Im}}, \tag{20}$$

Differentiating Eq. (20) with respect to x_α, then multiplying with $(\phi_{\zeta i}^{Re})^2$ and summing for all i, then repeating the procedure after replacing $\phi_{\zeta i}^{Re}$ by $\phi_{\zeta i}^{Im}$ and adding the two final equations and integrating, we arrive at the differential virial theorem for the "scaled" quantities

$$n(\mathbf{r})\frac{\partial v_{\zeta KS}}{\partial x_\alpha} = \frac{1}{4}\frac{\partial}{\partial x_\alpha}\nabla^2 n(\mathbf{r}) - 2\sum_\beta \frac{\partial}{\partial x_\beta}t_{\zeta\alpha\beta}, \tag{21}$$

where $t_{\zeta\alpha\beta}$ is the "scaled" non-interacting kinetic energy density tensor defined by

$$t_{\zeta\alpha\beta} = \frac{1}{4}\left[\frac{\partial^2}{\partial x'_\alpha \partial x''_\beta} + \frac{\partial^2}{\partial x'_\beta \partial x''_\alpha}\right]\gamma_\zeta(\mathbf{r}';\mathbf{r}'')|_{\mathbf{r}'=\mathbf{r}''=\mathbf{r}}. \tag{22}$$

The "scaled" first-order non-interacting density matrix γ_ζ can be expressed with the "scaled" orbitals as

$$\gamma_\zeta(\mathbf{r},\mathbf{r}') = \zeta\sum_i \lambda_i\phi_{\zeta i}^*(\mathbf{r})\phi_{\zeta i}(\mathbf{r}'). \tag{23}$$

$t_{\zeta\alpha\beta}$ is a real, symmetric tensor. The trace of $t_{\zeta\alpha\beta}$ gives the "scaled" non-interacting kinetic energy density t_ζ that integrates to the "scaled" non-interacting kinetic energy

$$T_\zeta = \int \sum_\alpha t_{\zeta\alpha\alpha}(\mathbf{r})d\mathbf{r} = \int t_\zeta(\mathbf{r})d\mathbf{r}\ . \tag{24}$$

The differential virial theorem (21) can be rewritten as

$$\nabla v_{\zeta KS} = -\mathbf{f}_{\zeta KS} \tag{25}$$

where the force field $\mathbf{f}_{\zeta KS}$ is defined

$$\mathbf{f}_{\zeta KS} = \frac{-\frac{1}{4}\nabla\nabla^2 n(\mathbf{r}) + \mathbf{z}_{\zeta KS}}{n(\mathbf{r})}. \tag{26}$$

The definition of the vector field $\mathbf{z}_{\zeta KS}$

$$\mathbf{z}_{\zeta KS} = 2\sum_{\beta} \frac{\partial}{\partial x_\beta} t_{\zeta\alpha\alpha} \tag{27}$$

is the divergence of the "scaled" non-interacting kinetic energy density tensor.

The form (25) of the differential virial theorem can be considered as a differential equation for the "scaled" Kohn-Sham potential and can be solved as

$$v_{\zeta KS}(\mathbf{r}) = \int_{\infty}^{\mathbf{r}} \mathbf{r}' \cdot \mathbf{f}_{\zeta KS}(\mathbf{r}'), \tag{28}$$

where $v_{\zeta KS}(\infty) = 0$ was utilized. Making use of the partition of the "scaled" Kohn-Sham potential (8), the unknown part of $v_{\zeta KS}$, the "scaled" exchange-correlation potential $v_{\zeta xc}$ can be obtained from Eq. (28). This equation can be used to check the accuracy of an approximate potential.

V. DISCUSSION AND ILLUSTRATION

The forms of the virial theorem derived here for the "scaled" system are significant from conceptual and practical points of view. Exact relations and theorems play a very important role in the density functional theory as they proved to be useful in improving the accuracy of approximate energy functionals. In the Kohn-Sham scheme exchange can be treated almost exactly via the optimalized potential (OPM) [21] and the Krieger-Li-Iafrate (KLI) [22] approaches. Only the correlation part of the Kohn-Sham potential should be approximated. It is, however, a very difficult task. As it was shown in [4] density scaling provides an approximation. It turned out that there exists a value of the scaling factor (ζ_c) for which the "scaled" correlation energy disappears: $E_{c\zeta_c} = 0$, that is, the "scaled" exchange-correlation energy is equal to the "scaled" exchange energy: $E_{xc\zeta_c} = E_{x\zeta_c}$. The "scaled" exchange energy $E_{\zeta x}[\varrho]$ is defined by the Hartree-Fock like expression [5]

$$E_{\zeta x}[\varrho] = -\frac{1}{2}\int \frac{|\gamma_\zeta(\mathbf{r}_1, \mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \tag{29}$$

where the "scaled" non-interacting one-particle density matrix is given by Eq. (23). Both the OPM and the KLI methods were derived for the "scaled" quantities [5]. The ζKLI approximation for the "scaled" exchange potential is

$$v_{\zeta x} = v_{\zeta S} + \frac{\zeta}{\varrho} \sum_{i=1}^{M} \langle \phi_{\zeta i} | \lambda_i v_{\zeta x} - v_{\zeta x,i} | \phi_{\zeta i} \rangle |\phi_{\zeta i}|^2 \ , \tag{30}$$

where

$$v_{\zeta S} = \frac{\zeta}{\varrho} \sum_{i=1}^{M} \phi^*_{\zeta i} v_{\zeta x,i} \phi_{\zeta i} \tag{31}$$

is the "scaled" Slater potential and

$$v_{\zeta x,i}(\mathbf{r}) = \frac{\delta E_{\zeta x}[\phi_{\zeta i}]}{\phi_{\zeta i} \delta \phi^*_{\zeta i}} \tag{32}$$

is the orbital dependent (Hartree-Fock-like) exchange potential. Note that for $\zeta = 1$ Eq. (30) gives the original KLI exchange potential.

The values of the scaling factor (ζ_c) for which the ζKLI total energy equals to the exact energy were calculated for several atoms [5]. It should be emphasized, however, that the "scaled" correlation potential is not zero, though the "scaled" correlation energy disappears. Therefore, the virial of the "scaled" correlation potential is also different from zero. So the "scaled" Levy-Perdew relation (19) cannot be rewritten with the "scaled" exchange potential

$$T_{\zeta_c c} + E_{\zeta_c x} + \int \varrho \mathbf{r} \cdot \nabla v_{\zeta_c x}(\mathbf{r}) d\mathbf{r} \neq 0 \ . \tag{33}$$

The deviation of the left hand side of the "scaled" Levy-Perdew relation (33) from zero provides a test of the ζKLI method. Table I shows the values of the ζ_c for which the ζKLI total energy equals to the exact energy (also presented in the Table) and the left hand side of the "scaled" Levy-Perdew relation (33). As it is expected the latter values are not zero, but they are small showing that the ζKLI method can be a suitable approximation for several applications.

In conclusion, we can state that density scaling is a very powerful technique. The virial theorem and the differential virial theorem are derived for the scaled system. As there exists a value of the scaling factor for which the correlation energy disappears and the exchange can be treated by a generalized OPM or KLI method, a simple approximation with only one parameter can be generated. The virial theorem is applied to judge the quality of the approximation.

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Table I

The values of ζ_c, the exact total energy and $T_{\zeta_c c} + E_{\zeta_c x} + \int \varrho \mathbf{r} \cdot \nabla v_{\zeta_c x} d\mathbf{r}$ calculated with the ζKLI method at ζ_c (in Ry).

atom	ζ_c	E_{exact}	$T_{\zeta_c c} + E_{\zeta_c x} + \int \varrho \mathbf{r} \cdot \nabla v_{\zeta_c x} d\mathbf{r}$
Be	1.01004	-29.334	-0.012
B	1.00766	-49.300	0.002
F	1.00545	-199.432	0.008
Ne	1.00540	-257.852	-0.018
Na	1.00406	-324.480	0.024
Mg	1.00350	-400.048	0.030
Al	1.00290	-484.590	0.021
Cl	1.00189	-920.008	0.035
Ar	1.00191	-1054.776	-0.026